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Leach Behaviour of RBMK-1500 Graphite

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Document title

Leach Behaviour of RBMK-1500 Graphite

Executive summary

The first results of short-term leaching test of 2 samples of grade GR-280 graphite bushings from the RBMK-1500 reactor (water-cooled graphite-moderated reactor) are presented in this report.

The leaching test of ^{14}C from irradiated graphite bushing of INPP RBMK-1500 reactor (Unit 1) has been planned according to the ISO method of leach testing of immobilized radioactive waste solids.

For the test two alkaline leaching solutions (pH=7.5 and pH=10) have been prepared by addition controlled amount of NaOH to distilled water.

The leached amount of ^{14}C after one day soak in alkaline water solution corresponds to ≈ 0.02 % of the total ^{14}C activity.

Leaching rate for both samples during the first day comparing with leaching rate during the first week is about two times higher. It means that there are two fractions of ^{14}C in the irradiated graphite, one of which is loosely trapped. Nitrogen is used to flush the graphite stack of the RBMK reactors therefore it can be expected that its activation reaction mostly occurs on the surface. This fact enables to suppose that loosely trapped fraction of ^{14}C is due to presence on the surface of irradiated graphite weakly bounded ^{14}C atoms that were produced in the reaction $^{14}N(n,p)^{14}C$.

The results that come out from this task are necessary for implementation of Work Package 6.

Revisions

Rev.	Date	Short description	Author	Review	Task Leader	WP Leader
01	30/05/2013	Final report	G. Duškesas FTMC	A. Plukis FTMC	J. Comte CEA	B. Grambow SUBATECH

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1 Introduction

Ignalina NPP consists of two Units with RBMK-1500 water-cooled graphite-moderated channel-type power reactors. Unit 1 was shut down at the end of 2004 while Unit 2 was shut down in the end of 2009.

Cross section of RBMK-1500 reactor vault is presented in Fig. 1 [1].

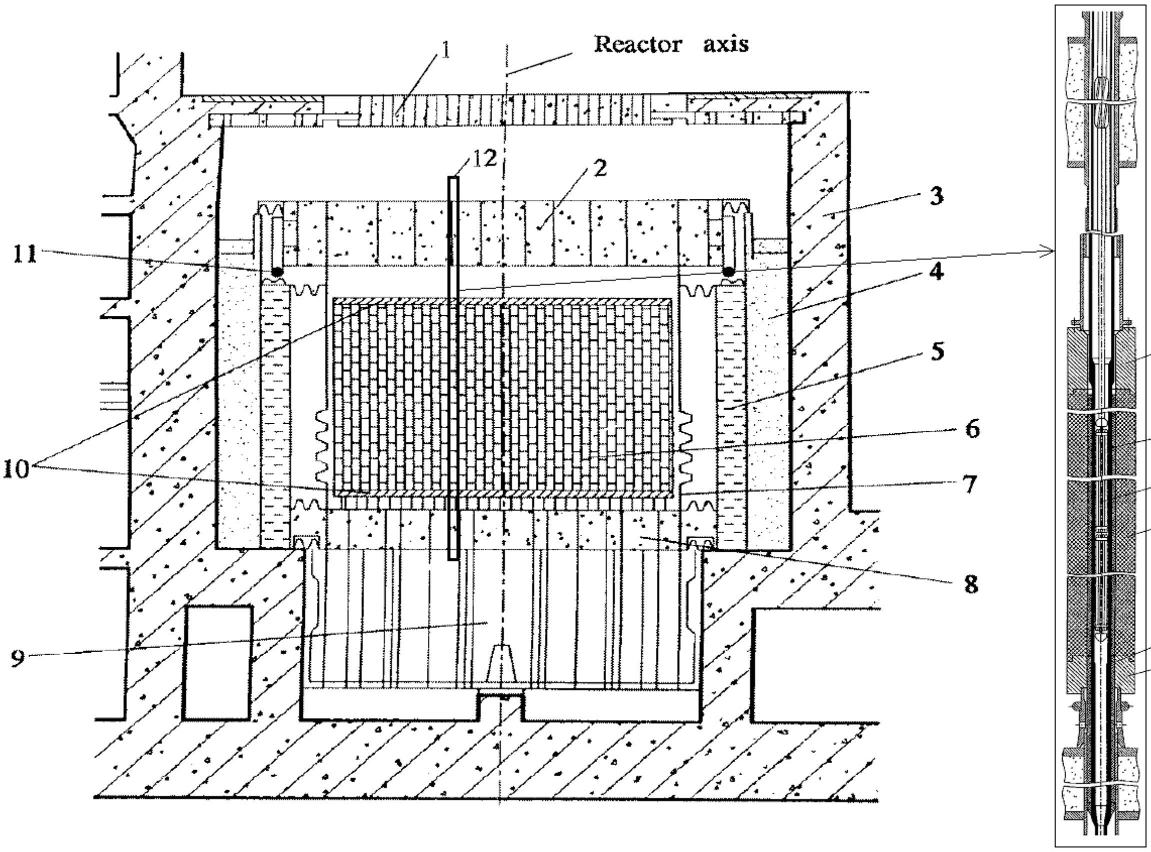

Fig. 1. Cross–section of RBMK–1500 reactor vault [1]

1 – top cover (floor of the central hall);	7 – reactor shell;	13 – shield plate;
2 – top metal structure (with serpentinite);	8 – bottom metal structure (with serpentinite);	14 – FC central part;
3 – concrete vault;	9 – reactor support structure;	15 – FA inside FC;
4 – sand cylinder;	10 – steel shield and support plates;	16 – graphite blocks;
5 – water tank;	11 – roller supports;	17 – graphite rings/sleeves;
6 – graphite stack;	12 – modelled segment;	18 – support plate

The graphite stack (6) serves as a neutron moderator and reflector. The graphite stack consist of individual graphite blocks (16) made of GR-280 grade graphite, and can be visualized as a vertical cylinder, made up of 2488 graphite columns (8 m height), constructed from different types of graphite blocks and bushings. The upper and the lower 0.5 m thick graphite stack layers are called respectively top and bottom reflectors as there is no fuel in these regions and graphite is mainly used here for neutron reflection back to the active core. The blocks are rectangular parallelepipeds, with a base of 0.25 × 0.25 m, and heights of 0.2, 0.3 and 0.6 m. The blocks have a 0.114 m diameter bore openings through the vertical axis, and this provides a total of 2044 fuel (technological) channels (14) which are used for placing fuel assemblies (15), control rods and other equipment into the core. The openings in the remaining 444 peripheral graphite columns are filled with graphite rods in order to increase neutron reflection and these columns serve as radial reflector. In order to improve heat transfer from the graphite stack, the central segment of the fuel channel is surrounded by the 0.02 m high and 0.0115 m thick split GRP-2-125 grade graphite rings (17). These rings are arranged next to one another in such a manner that one is in contact with the channel, and the other with the graphite stack block. Above and below graphite rings there are also placed GRP-2-125 grade graphite sleeves of different shape compared to the rings. The graphite stack, including its hermetically sealed cavity, is called the sealed reactor space. This space is filled with a circulating helium-nitrogen mixture at an excess pressure of 0.49–1.96 kPa.

During reactor operation graphite blocks, bushings and rings/sleeves are under intensive neutron irradiation and became activated. The neutron activation conditions (20 years of irradiation of the same material with the same intensity of neutron flux) of graphite bushings are similar to ones of graphite blocks. From the point of view of graphite waste radiological characteristics graphite bushings are representative for entire RBMK-1500 graphite stack.

The first results of short-term leaching test of GR-280 grade graphite bushings are presented in this report.

2 Sampling

Sampling of grade GR-280 graphite bushings from graphite stack of RBMK-1500 reactor of Unit 1 has been completed by Ignalina NPP staff by July 2012.

Samples for the leaching test of RBMK-1500 reactor graphite have been prepared by Ignalina NPP staff from graphite bushing No. 6-51 (weight 228 g) by dividing it into 8 parts in February of 2013 (see Fig. 2).

For the leaching test the sample No. 1 (sample of type L3, located between cut 1 and cut 3 lines), and sample No. 4 (sample of type L3, adjacent to sample No.1) have been chosen. Weight of samples No. 1 and No. 4 is equal to 13.9682 g and 15.6917 g., respectively.

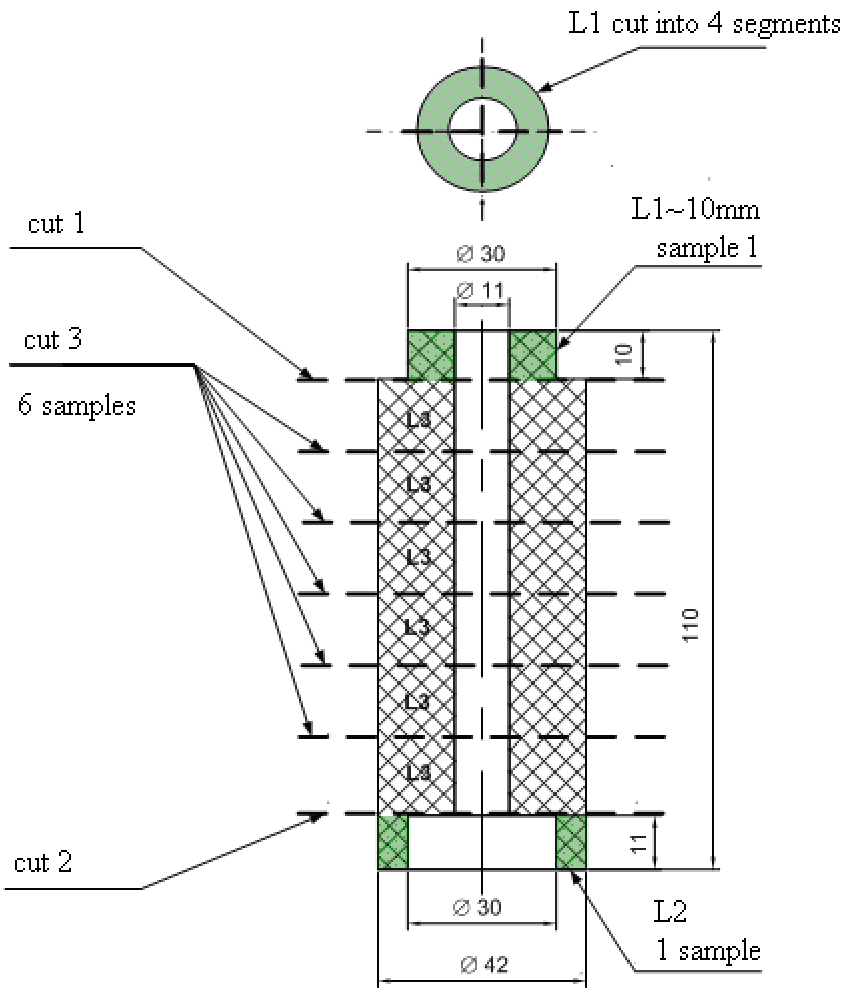

Fig. 2. Division of graphite bushing No. 6-51 into eight parts

3 Leaching test setup

The leaching test of ^{14}C from irradiated graphite bushing of INPP RBMK-1500 reactor (Unit 1) has been planned according to the standard method of leach testing of immobilized radioactive waste solids [2].

The leachate volume V_L to sample geometrical surface S was 10:1. Prior to leaching, graphite samples were cleaned by immersing them in 200 mL of demineralized water for 1 to 2 minutes to remove dust. Then graphite samples were immersed into the acetone for 5-7 sec and desiccated at room temperature. With that they were completely immersed in the alkaline leaching solution in closed but not leak-proof containers. Alkaline leaching solution was prepared by addition controlled amount of NaOH to distilled water.

Testing frequency employed was once daily (one week) then once weekly every eight weeks, then monthly as deemed appropriate. After the fixed intervals the leaching solutions were poured off completely and graphite was poured with fresh solution again. The portion of 100 mL was taken for the radiochemical separation of ^{14}C. Summary of leaching test conditions is presented in Table 1.

Table 1. Summary of leaching test conditions

Sample No.	1	4
Type of test	Static	Static
Temperature	Room temperature	Room temperature
Duration	60 days	60 days
Testing frequency	Daily Weekly Monthly	Daily Weekly Monthly
Sample type	Solid	Solid
Graphite mass, g	13.9682	15.6917
Sample surface, mm^2	2706.5	2898.6
Leaching solution	Distilled water	Distilled water
Initial pH	7.5	10

Until now very short-term test has only been carried out due delay of preparation of samples for the leaching test by Ignalina NPP.

4 Determination of radiocarbon in leaching solution

^{14}C is a pure beta emitter which decays by emitting β-particles with the maximum energy of 156 keV; it can therefore be measured by beta counting, mainly liquid scintillation counting. In this method, ^{14}C is prepared as a liquid sample and then measured. The very often used method for the analysis of waste sample is acid digestion, in this case all forms of carbon is converted to CO_2 and absorbed in alkaline solution, which is mixed with scintillator cocktail for the LSC.

The procedure has been applied to determine ^{14}C in graphite. ^{14}C has been effectively removed from matrix in form of CO_2 by treating the sample with concentrated (H_2SO_4:HNO_3: $HClO_4$ =15:4:1) acid and hydrogen peroxide. Carbon dioxide is passed through solution of sodium hydroxide to form sodium carbonate. The part of solution is transferred to a liquid scintillation vial containing an appropriate cocktail and counted using a liquid scintillation analyser [3].

4.1 Procedure

Basic installation for ^{14}C extraction procedure is shown in Fig. 3

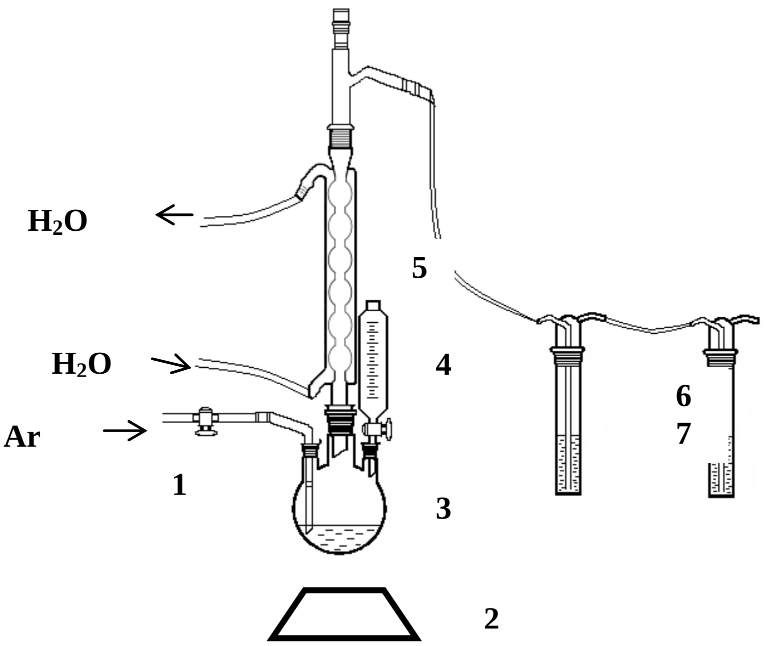

Fig. 3. Basic installation for ^{14}C extraction procedure: 1 - feeding of Ar; 2 – electric plate; 3 – three-necked round flask; 4 – separating funnel; 5 – condenser; 6 and 7 – gas washing bottles

All chemicals used were of analytical-reagent grade.

Steps of procedure for ^{14}C extraction from were [4]:

1. Transfer of an appropriate aliquot of sample in a three-necked round flask. If it was necessary, moderate quantity of distilled water to avoid overheating of flask was added;
2. Placement of a three-necked round flask on an electric plate and sick up to the stand base;
3. Joint of a flask with the condenser and separating funnel;
4. Joint of a condenser with gas washing bottles;
5. Addition of 50 ml 3M NaOH into each gas-washing bottle and joint the bottle with condenser;
6. Addition of 50 ml of the mix of concentrated acids to separating funnel;
7. Switch on an electric plate. Switch on argon. When the sample comes to the boil, start drips the concentrated acids;
8. Addition of 25 ml of H_2O_2 to separating funnel and start drip it;
9. Repetition of steps 5 and 7 2-3 times while the sample decompose;
10. Waiting until a flask cooled to room temperature;
11. Disconnection of a gas washing bottles from condenser;
12. Transfer of an aliquot of 4 ml of Na_2CO_3 solution from first gas washing bottle to a liquid scintillation vial;
13. Addition of 16 ml of the scintillator Optiphase HiSafe 3 to a vial, cap, shake well, and allow the mix to stay for at least one hour before submitting for counting.

4.2 Calibration

For counting efficiency, a ^{14}C-ARU-1 standard is used. An uncertainty of standard solution is 3 %. An average counting efficiency of ^{14}C in the preparation of Na_2CO_3 is 40 %.

4.3 Calculations

The following equation defines the specific activity value of ^{14}C.

$$A_{C14} = \frac{(N - N_F) \bullet V_2}{60 \bullet \varepsilon \bullet V_1 \bullet m}$$

A_{C14} - specific activity of ^{14}C, Bq/kg

N - counting rate, cpm

N_F - counting rate of background, cpm

ε - counting efficiency, cpm/dpm

V_1 - sample (Na_2CO_3) volume, L

V_2 - total volume of Na_2CO_3, L

m - sample mass, kg

5 Results and discussion

The first results of the leaching test of irradiated RBMK-1500 graphite bushings in two alkaline water solutions are presented in the Table 2.

Table 2. Activity of ^{14}C (Bq) from the graphite GR-280 bushings samples in a alkaline water solution as a function of leaching time

t, days	Distilled water, pH 7.5		Distilled water, pH 10	
	Blank	Sample No. 1 (13.9682 g)	Blank	Sample No. 4 (15.6917 g)
1	<0.3 Bq	10.8 ±1.0 Bq	<0.3 Bq	11.6 ±1.0 Bq
7	<0.3 Bq	3.8 ±0.4 Bq	<0.3 Bq	6.0 ±0.6 Bq

Total measured ^{14}C activity of sample No. 1 is 48 000 ± 4 000 Bq. This results in specific activity equal to 1.71E+05 ± 1.4E+04 Bq/g.

^{14}C is produced in the reactor graphite due to three neutron reactions: $^{13}C(n, \gamma)^{14}C$, $^{14}N(n, p)^{14}C$, and $^{17}O(n, \alpha)^{14}C$. The first two reactions are much more important than the last one. Simulation of the carbon irradiation in a nuclear reactor can be done with high enough accuracy contrary to simulation of the reaction $^{14}N(n, p)^{14}C$. Thus it is worth only to compare directly the measured results with the calculated ones from the reaction $^{13}C(n, \gamma)^{14}C$.

20 years of neutron activation of graphite stack of RBMK-1500 reactor simulation by MCNPX code (for simulation details see [5]) of the reaction $^{13}C(n, \gamma)^{14}C$ results in ^{14}C specific activity equal to 7.17E+04 Bq/g. The simulated specific activity value is about two times lower than the measured one. The difference between the measured specific activity and the specific activity simulated from the $^{13}C(n, \gamma)^{14}C$ reaction can be attributed to the yield of the reaction $^{14}N(n, p)^{14}C$.

The leached amount of ^{14}C from the sample No. 1 after one day soak in alkaline water solution corresponds to ≈ 0.02 %. Such leaching rate is in correspondence with other irradiated graphite leaching tests [6-9].

An interesting feature of leaching dynamics is a bigger leaching rate at the leaching beginning. Results in Table **3** show about twice higher leaching rate for both samples during the first day comparing with leaching rate during the first week. It means that there are two fractions of ^{14}C in the irradiated graphite, one of which is loosely trapped.

The reason of being of two different ^{14}C fractions in the irradiated graphite can be related with the two main paths of ^{14}C generation in a nuclear reactor resulting in two different preferable locations of for ^{14}C atoms at graphite lattice.

Nitrogen is used to flush the graphite stack of the RBMK reactors therefore it can be expected that its activation reaction mostly occurs on the surface (30 nm according to ref. [11]) of graphite where non-negligible amount of ^{14}N from cooling gas of the core cooling gas circuit can be accumulated. The impurities of ^{14}N in the graphite stack comprise 0.5 – 70 ppm as reported in [10]. Taken into account this concentration the amount of ^{14}C produced in the reaction $^{14}N(n,p)^{14}C$ has been calculated by MCNPX code in a similar way as in the case of reaction $^{13}C(n,\gamma)^{14}C$ considering appropriate macroscopic cross-sections. The lowest ^{14}N concentration range corresponds to an increase of ^{14}C activity by 18%, and the highest range – an increase even 25 times. The measured value of ^{14}C activity is about 2 times higher compared with the simulated one from the reaction $^{13}C(n,\gamma)^{14}C$. This makes attribution of the difference between the measured ^{14}C activity and simulated activity due to the reaction $^{13}C(n,\gamma)^{14}C$ to the yield of the reaction $^{14}N(n,p)^{14}C$ reasonable.

6 Conclusions

Beta spectrometric measurements of activity of ^{14}C from the graphite GR-280 bushings gives specific activity equal to 1.71E+05 ± 1.4E+04 Bq/g.

The leached amount of ^{14}C after one day soak in alkaline water solution corresponds to ≈ 0.02 % of the total ^{14}C activity.

Leaching rate for both samples during the first day comparing with leaching rate during the first week is about two times higher. It means that there are two fractions of ^{14}C in the irradiated graphite, one of which is loosely trapped. Nitrogen is used to flush the graphite stack of the RBMK reactors therefore it can be expected that its activation reaction mostly occurs on the surface. This fact enables to suppose that loosely trapped fraction of ^{14}C is due to presence on the surface of irradiated graphite weakly bounded ^{14}C atoms that were produced in the reaction $^{14}N(n,p)^{14}C$.

7 References

1. Almenas, K.; Kaliatka, A.; Uspuras, E. 1998. *Ignalina RBMK-1500: A source book, 2nd ed.* Kaunas, Lithuania: Lithuanian Energy Institute.
2. International Standards Organization (ISO), Long-term leach testing of radioactive waste solidification products. ISO/TC 85/SC 5/WG 38, 1979.
3. Gudelis, A.; Gvozdaitė, R.; Lukoševičius, Š. 2009. On determination of radiocarbon leakage from a shallow-land radioactive waste repository. *LSC 2008, Advances in Liquid Scintillation Spectrometry*: 415-420. Tucson, USA: Radiocarbon.
4. Hou X, Rapid analysis of ^{14}C and ^{3}H in graphite and concrete for decommissioning of nuclear reactor. Applied Radiation and Isotopes 62 (2005) 871–882.
5. Norkūnas E., Šmaižys A., Poškas P., Druteikienė R., Duškesas G., Garbaras A., Gudelis A., Gvozdaitė R., Lujanienė G., Plukienė R., Plukis A., Puzas A., I. M. 2002. Assessment of Isotope-Accumulation Data from RBMK-1500 Reactor. Technical Report T-3.4.2, CARBOWASTE-1105-T-3.4.2.
6. Hespe, E.D., Leach testing of immobilised radioactive waste solids: a proposal for a standard method. Atomic Energy Review, 1971. 9: p. 195-207.
7. Gray, W.J. and W.C. Morgan, Leaching of ^{14}C and ^{36}Cl from Hanford Reactor Graphite, P.N. Labs, Editor. 1988.
8. Gray, W.J. and W.C. Morgan, Leaching of ^{14}C and ^{36}Cl from irradiated french graphite, P.N. Labs, Editor. 1989.
9. White, I.F., et al., Assessment of graphite management modes for graphite form reactor decommissioning, in CEC, E. Commission, Editor. 1984.
10. Ancius D., Ridikas D., Remeikis V., Plukis A., Plukiene R., Cometto M., Evaluation of the activity of irradiated graphite in the Ignalina Nuclear Power Plant RBMK-1500 reactor, Nukleonika 50 (2005) 113–120.
11. Takahashi R., Toyahara M., Maruki S., Ueda H., Investigation of morphology and impurity of nuclear grade graphite and leaching mechanism of Carbon-14, in: Nuclear Graphite Waste Management, Proc. of IAEA Technical Committee meeting held in Manchester, U.K, 18-20 October 1999, IAEA, Vienna, 2001, pp. 176-190.